Journal of Nuclear Materials 446 (2014) 117–123

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Corrosion susceptibility of EUROFER97 in lithium ceramics breeders

Teresa Hernández *, Pilar Fernández, Rafael Vila

National Laboratory for Magnetic Fusion, CIEMAT, Madrid, Spain

ARTICLE INFO

Article history:
Received 15 April 2013
Accepted 30 November 2013
Available online 7 December 2013

ABSTRACT

EUROFER97 specimens were exposed in vacuum to lithium silicate pebbles at 550 °C for up to 2880 h, to evaluate its corrosion susceptibility in a simulated breeder blanket environment. The specimens and pebble bed were then analyzed and characterized by SEM-EDX, XRD, and HR-TEM. The results revealed the formation of a double chromium/iron oxide corrosion layer. HR-TEM also showed that the inner layer was amorphous, while the outer was crystalline. The amorphous layer was brittle, broke easily, and became detached from the steel.

1. Introduction

In the framework of the European Union fusion power development programme, two tritium breeding blanket concepts were selected as reference for the future demonstration power plant (DEMO) [1]. For more than a decade the fusion materials community has been working on the design of the helium cooled pebble blanket (HCPB) and helium cooled lithium lead (HCLL) concepts, both of which present many common design features. Both use lithium as the tritium breeder, the HCPB concept using a lithium containing ceramic in pebble bed form with Be as neutron multiplier, while the HCLL uses eutectic Li–Pb flowing at low velocity for tritium recovery purposes. Two different ceramic breeder pebbles have been developed, produced, and qualified: lithium orthosilicate (Li_4SiO_4) and lithium metatitanate (Li_2TiO_3) [2]. Within the nuclear fusion community, lithium ceramic breeders are referred to fertile material that after bombarding by neutrons is transformed in tritium, which will be used as fuel.

Reduced activation ferritic/martensitic steels (RAFMs) are the primary candidates as structural materials for the breeding blankets, and in particular the EUROFER97 specially developed for fusion structural applications. This material has been selected for the two European blankets designs [3,4], and its thermal and mechanical behavior has been extensively investigated for many years [5,6].

At present there is considerable research concerned with the corrosion of RAFM steels in liquid breeders (Li–Pb) [7,8], however no comparable activity for solid breeders is underway, the closest being a compatibility study of lithium ceramics and stainless steels [9]. Also although silicate solutions have been used as corrosion inhibitors for iron for a long time [10,11], there is no information about the effect for such compounds in anhydrous environments or vacuum. Although it is expected that the degradation caused by solids will be less than that due to liquid Li–Pb, it is not negligible and must be evaluated properly. This is particularly true if one takes into account the important safety implications of failure due to potential tritium release.

The objective of this work is to perform a systematic study of corrosion processes for the candidate steel in order to evaluate its compatibility with Li_4SiO_4. EUROFER97 specimens, covered with lithium silicate powder, were tested under expected working conditions; 550 °C in vacuum. Specimens were removed at increasing times up to 2880 h, in order to investigate the corrosion process and evolution as a function exposure time. Although the weight change was negligible during the tests, the microstructural SEM/EDX and optical examinations indicate a corrosion attack that could be attributed to an exfoliation process. In addition, an exhaustive chemical analysis of the solid breeder material and the steel was performed before and after testing, to identify the transferred species between the steel to the breeder material.

2. Materials and method

The lithium silicate was obtained in our laboratory by the spray drying technique followed by pyrolysis [12]. Stoichiometric amounts of lithium and siliceous acetates of analytical grade were used as raw materials. Weight changes during heating the mixture were investigated by thermogravimetric analysis with a 10°/min heating rate from RT to 1000° in air. Typical TG curves showed that a weight loss of about 30% occurred for temperatures below 600°, with significant weight loss taking place at 550° (Fig. 1). Above about 600 °C the overall weight of the sample remained constant until 950° as shown by the TG analysis. Chemical thermodynamics indicates that a reaction proceeds when the Gibbs free-energy change is negative. The data given by Feng et al. [13] for Li_4SiO_4

---

* Corresponding author. Address: National Laboratory for Magnetic Fusion, Materials Department, CIEMAT, Avenida Complutense 40, Edif.2, Madrid 28040, Spain. Tel.: +34 91496 2581.

E-mail address: teresa.hernandez@ciemat.es (T. Hernández).

0022-3115/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnucmat.2013.11.047

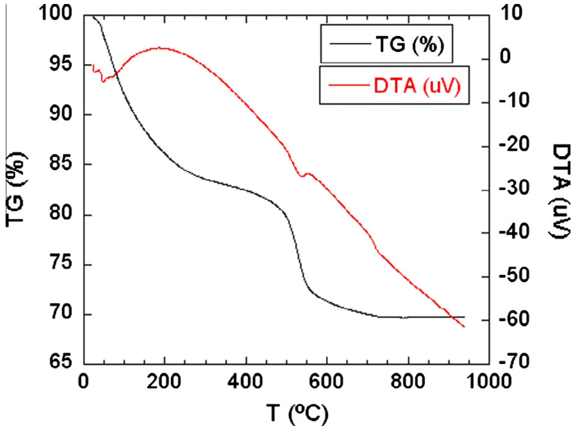

Fig. 1. DTA/TG of the lithium orthosilicate.

formation shows that it is an endothermic reaction between 500 °C and 1200 °C and the Gibbs energy in less than zero above 500 °C, in agreement with these results. After drying, the powder obtained was heated to 1000 °C to reach the orthosilicate phase, later identified by XRD and its morphology observed by SEM.

The steel investigated was the reduced activation ferritic/martensitic EUROFER97 with the following chemical composition (wt%): 0.11 C, 8.7 Cr, 1 W, 0.10 Ta, 0.19 V, 0.44 Mn, 0.004 S, balance Fe (Ciemat analyses). The steel was supplied as plates in the normalized (980 °C/27′) plus tempered (760 °C/90′/air-cooled) condition, referred to in this paper as the "as-received" material. Rectangular samples were cut and ground with up to 600 SiC paper-grit (equivalent to 26 μm roughness approximately) to $14 \times 5 \times 5$ mm^3 in all the cases. Before testing, the samples were cleaned using ethanol in an ultrasonic bath, dried and weighed. For the corrosion testing, the samples were buried in lithium silicate powder in an alumina crucible and introduced into a tubular furnace. The tests were performed in vacuum ($\sim 3.10^{-3}$ bar) at 550 °C for 168, 336, 720, 1440 and 2880 h. Equivalent times and temperature conditions, but without the lithium silicate, were used to prepare reference samples.

2.1. Characterization

After testing, the specimens were cleaned in deionized water, measured and weighed. Metallographic studies on polished and etched surfaces were performed on the cross section for all samples by SEM (JEOL Mod. JSM 6400 EDX) and FG-SEM (JEOL). The corrosion products were analyzed by XRD (PANalytical mod. X'Pert PRO MRD) to determine the oxide type formed. Focused ion beam (FIB) micro-processing was used for the preparation of TEM (JEOL Mod. 3000F) specimens; each thin foil including corrosion layer and base material. Energies from 30 kV to 2 kV were used for the Ga ion beam. The FIB lamellas were observed using HR-TEM (JEOL) operating at 300 kV.

3. Results

3.1. Microstructure of EUROFER97

The initial treatment produces a fully martensitic structure with lath-shaped martensite subgrains of about 0.5 ± 0.2 μm. Fig. 2 shows representative SEM and TEM micrographs of this steel for the as-received state. As can be seen, the EUROFER97 presents a fine structure with an ASTM prior austenite grain size in the range from 10 to 11.5 (6.7–11 μm). The tempering treatment produced large amounts of carbide precipitation distributed preferentially along grain and lath boundaries. Moreover precipitates appeared also in the bulk of the martensite lathes. The main precipitates consisted of $M_{23}C_6$ particles of variable size (25–210 nm) located preferentially along grain and lath subgrain boundaries. In the as-received state, other types of precipitates (MX type) rich in Ta or V, with a size from 8 to 40 nm, were identified. These were mainly located inside the subgrains. A detailed microstructural characterization by optical, SEM and TEM of the EUROFER97 steel for the as-received condition is described in [14,15].

3.2. Corrosion layers

The metallographic results after corrosion tests in Li_4SiO_4 at 550 °C have shown changes in the surface relative to the reference samples. The SEM results showed uniform corrosion attack over the entire exposed surface, but with weak adherence of the corrosion layer to the steel leading to cracking. The thickness of the corrosion layer was measured in different points on polished surfaces of the metallographic samples. The measurements performed have not shown a significant growth of the oxide layer as the testing time increased (Fig. 3), with the corrosion scale thickness increasing from 490 nm (168 h) to 700 nm (2880 h). It is worth to point out that the thickness values determined in this work must only be considered as an estimate due to the brittle nature of the layer and its poor adhesion to the steel, which produced a loss of corrosion product during metallographic preparation. Examination of the samples also revealed that the corrosion layer

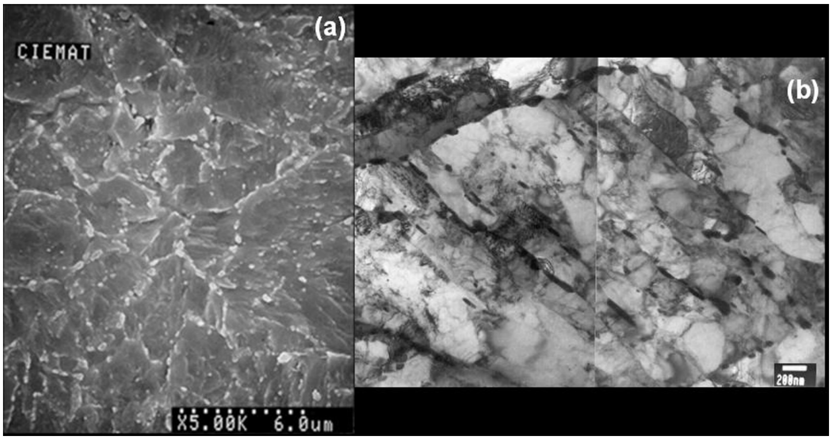

Fig. 2. General microstructure by SEM (a) and TEM (b) of Eurofer'97 steel on as-received condition (normalized at 980 °C/27′ plus tempered at 760 °C/90′/air-cooled).